

PTO 05-1054

CY=JA DATE=19790116 KIND=A  
PN=54-004997

THERMOSETTING RESIN COMPOSITION  
[Netsukoukasei jushi soseibutsu]

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translation of  
"JP 5404 997 A"  
(N on Form 892)

UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. December 2004

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	5404997
DOCUMENT KIND	(12):	A [PUBLISHED UNEXAMINED APPLICATION]
PUBLICATION DATE	(43):	19790116
APPLICATION NUMBER	(21):	52069848
APPLICATION DATE	(22):	19770615
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INTERNATIONAL CLASSIFICATION	(51):	C 08 G 73/02; C 08 G 59/40
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TITLE	(54):	THERMOSETTING RESIN COMPOSITION
FOREIGN TITLE	(54A):	NETSUKOUKASEI JUSHI SOSEIBUTSU

## SPECIFICATION

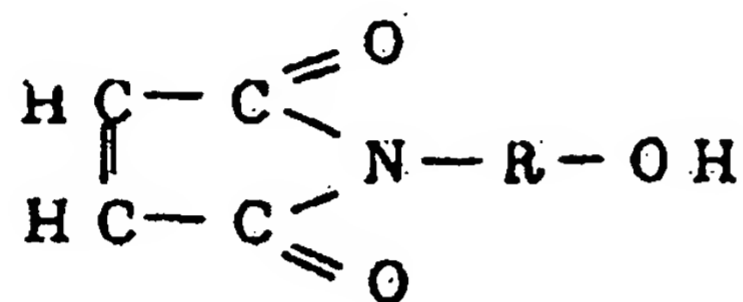
Title of the Invention

Thermosetting Resin Composition

Claims

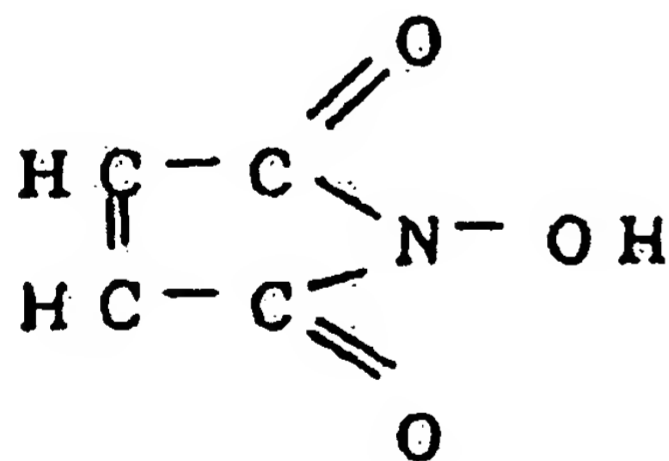
1. A thermosetting resin composition containing

(a) a reactant between epichlorohydrin and N-substituted maleimide that is expressed by



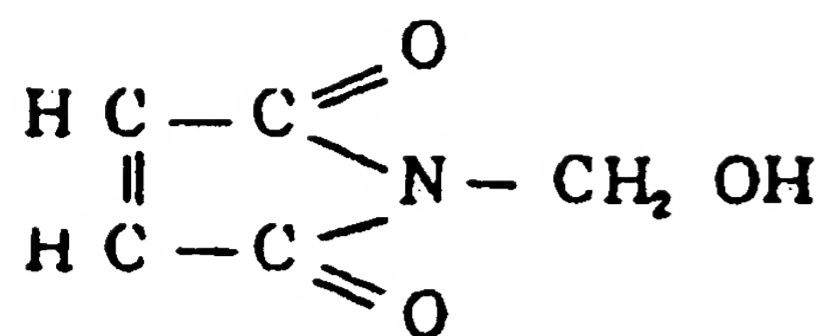
wherein R is  $-(\text{CH}_2)_n-$  or  $-\text{C}_6\text{H}_4-(\text{CH}_2)_m-$  (n and m are integers greater than or equal to 0) and  
(b) an amine compound.

2. A thermosetting resin composition of Claim 1 characterized by said general formula being

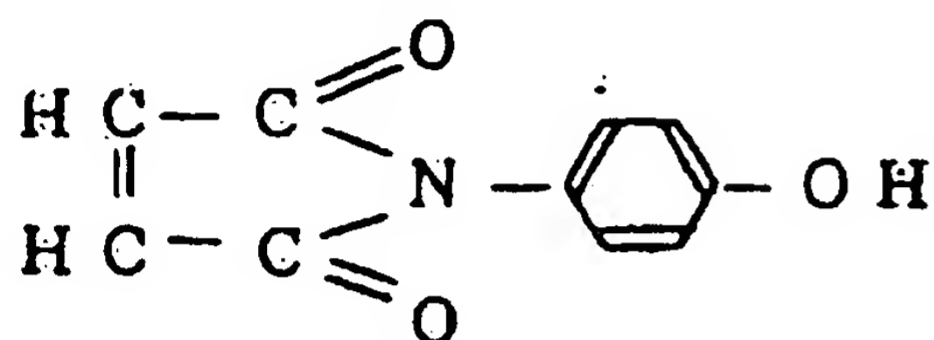


which is N-hydroxymaleimide.

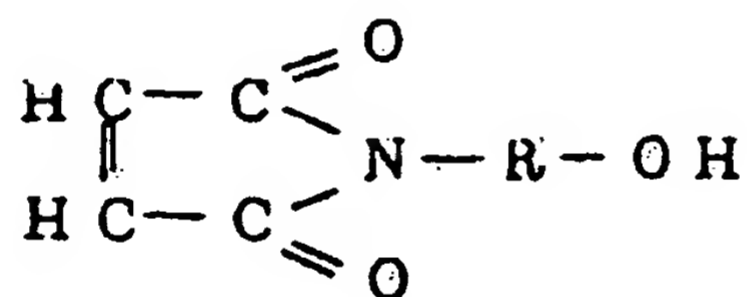
3. A thermosetting resin composition of Claim 1 characterized by said general formula being



4. A thermosetting resin composition of Claim 1 characterized by said general formula being



5. A thermosetting resin composition containing  
(a) a reactant between epichlorohydrin and N-substituted maleimide that is expressed by



wherein R is  $-(\text{CH}_2)_n-$  or  $-\text{C}_6\text{H}_4-(\text{CH}_2)_m-$  (n and m are integers greater than or equal to 0),

- (b) an amine compound, and
- (c) a polyfunctional epoxy compound.

#### Detailed Explanation of the Invention

The present invention pertains to new heat-resistant resin components with excellent heat resistance and fast-curing properties.

As the capacities are increased, the sizes and weights are reduced, and/or the reliabilities are improved in recent electric and electronic

apparatuses, the demand for insulating materials and sealing materials with excellent heat resistance is increasing.

As conventional heat-resistant resins, heterocyclic polymers such as polyimide and silicon resins are known.

However, many heterocyclic polymers are condensation types and have various problems in that they produce volatile portions when cured, in that they have poor formability, or in that a specific polar solvent needs to be used when they are used as varnishes. Their usages are particularly limited in the fields of molding materials, laminated materials, and powder materials.

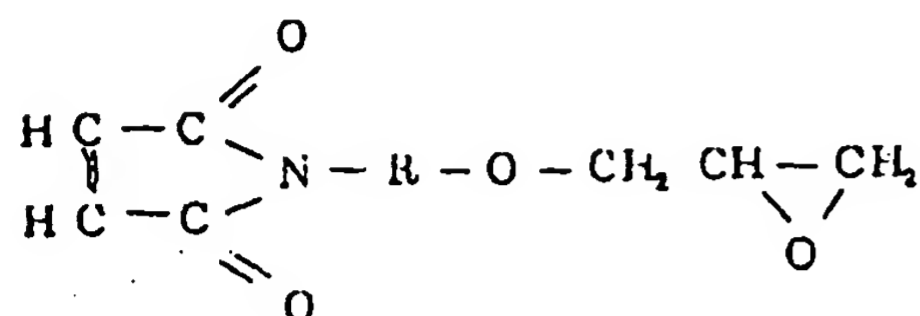
As for silicon resins, their usages are also limited since their mechanical strengths at high temperatures are low, since they have poor adhesion properties, and since their moisture permeabilities are high.

In order to remedy these shortcomings, bismaleimide, which is an addition-type imide, and an epoxy compound are used in combination.

However, even this mixture has problems in term of fast-curing properties and of solubility in various solvents, and these problems pose major hindrances when the mixture is used as a molding material, prepreg material, powder coating material, etc.

The present invention was completed in light of the above problems and its purpose is to supply a thermosetting resin composition that can be transformed into an indurative article with excellent high-temperature strength by simply being heated at a relatively low temperature (150~200°C) for a short time (1~30 minutes) and that has excellent solubility in solvents before being hardened.

Its key point is in a thermosetting resin composition that consists of: a reactant between N-substituted maleimide (see U.S.S.R. Patent No.508,501) and epichlorohydrin such as a reactant expressed by a formula



wherein R is  $-(\text{CH}_2)_n-$  or  $-\text{C}_6\text{H}_4-(\text{CH}_2)_m-$  (n and m are integers greater than or equal to 0); and an amine compound.

Conventional resin compositions obtained from bismaleimide and amine compounds or epoxy compounds have extremely poor solubilities in general solvents. A composition of the present invention, however, also has improved solubility in solvents.

Incidentally, in order to have satisfactory heat resistance and fast-curing properties, which are the characteristics of the present invention, the ratio between the epoxy equivalent of the reactant and the amine equivalent of the amine compound should be in a 1:0.3 ~ 3.0 range. If a polyfunctional epoxy compound is used and if the total epoxy equivalent is assumed to be 1, the ratio of the amine equivalent of the amine compound should be in a 0.3~3.0 range.

Moreover, the polyfunctional epoxy compound can be substituted up to 70 weight% of the reactant (a).

Although the hardening conditions vary depending on the composition, it is possible to obtain a target hardened material by molding it in a mold for 1~2 minutes at a hardening temperature of 150~200°C, by then

releasing it from the mold, and by then hardening it for 30 minutes or longer.

Incidentally, the reactant (a), which is an essential ingredient of the present invention, is obtained by heating and reacting epichlorohydrin and maleimide that is obtained by executing N-substitution using substitute groups containing OH groups for 1 hour at 80°C in the presences of an acidic compound and a basic compound such as sodium hydroxide, potassium hydroxide, etc.

The examples of the N-substituted maleimide of the present invention are N-hydroxymaleimide, N-(2-hydroxyethyl)maleimide, N-(2-hydroxyethyl)2,3-dimethylmaleimide, N-(hydroxymethyl)maleimide, N-(hydroxymethyl)2,3-dimethylmaleimide, N-(0-hydroxydipheynyl)maleimide, N-(P-hydroxyphenyl)maleimide, N-[P-(2-hydroxyethyl)sulfonyl]maleimide, etc., and at least one of these can be utilized.

Examples of the amine compound are aliphatic and aromatic amines such as monoethylamine, diethylamine, triethylamine, monoethanolamine, diethanolamine, phenylenediamine, benzyldimethylamine, pyridine, piperidine, phenyl containing 1~3 dimethylaminomethyl groups, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, hexamethylenetetramine modified aliphatic amine, polyamide, diethylaminopropylamine, diaminodiphenylmethane, diaminodiphenylsulfone, diaminodiphenylether, modified aromatic amine, dicyandiamide, urea, benzoguanamine, melamine, etc.

At least one of these compounds is utilized.

Moreover, diaminodiphenylmethane, diaminodiphenylsulfone, and diaminodiphenylether are particularly preferred for molding materials.

In the present invention, a polyfunctional epoxy compound indicates a compound containing oxirane rings inside the molecules, and the examples are bisphenol-A-diglycidylether, butadiene diepoxide, 3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexanecarboxylate, vinylcyclohexane dioxide, 4,4'-di(1,2-epoxyethyl)diphenylether, 4,4'-di(1,2-epoxyethyl)biphenyl, 2,2'-bis(3,4-epoxycyclohexyl)propane, resorcin diglycidylether, phloroglucin diglycidylether, methylphloroglucin diglycidylether, bis(2,3-epoxycyclopentyl)ether, 2-(3,4-epoxy)cyclohexyl-5,5'-spiro(3,4-epoxy)cyclohexane-m-dioxane, bis-(3,4-epoxy-6-methylcyclohexyl)adipate, N,N'-m-phenylenebis(4,5-epoxy-1,2-cyclohexane dicarboxyimide), hydantoin diepoxide, hydantoin trisepoxide, paraaminophenol triglycidyl compound, polyallyl glycidyl ether, 1,3,5-tri(1,2-epoxyethyl)benzene, 2,2',4,4'-tetraglycidoxybenzophenone, tetraglycidoxytetraphenylethane, polyglycidylether of phenol-formaldehyde novolac, triglycidylether of glycerol, triglycidylether of trimethylolpropane, etc.

Among these epoxy compounds, bisphenol-A-diglycidylether and the polyglycidylether of phenol-formaldehyde novolac, which are the most common compounds, are the most useful.

Moreover, one or more of the following different types of materials may be used in combination in addition to the composition of the present invention depending on various usages and purposes.

In other words, the following can be utilized for the purpose of obtaining a molding material: inorganic fillers such as zirconium, silica, fused silica glass, clay, alumina hydroxide, calcium carbonate, fused glass, glass, asbestos, calcium sulfate, magnesite, mica, kaolin, talc, graphite, cement, carbon iron, barium, ferrite, lead compound, molybdenum disulfide, zinc oxide, titanium white, carbon black, silica sand, wollastonite, etc.; mold-releasing agents such as ~~fatty acids or waxes;~~ and coupling agents such as epoxysilane, vinylsilane, borane compounds, alkoxy titanate compounds, etc.

Moreover, commonly-known fire-retarding materials comprised of antimony, phosphorus, etc. or plasticizers can be utilized as necessary.

Moreover, for the purpose of obtaining a varnish, a solvent can be utilized.

Examples of the solvent include: organic polar solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, N,N-diethylformamide, N-methylformamide, dimethylsulfoxide, N,N-diethylacetamide, N,N-dimethylmethoxyacetamide, hexamethylphosphamide, pyridine, dimethylsulfone, tetramethylenesulfone, dimethyl tetramethylenesulfone, etc.; phenol solvents such as phenol, cresol, xylenol, etc.; and ketones such as methylethylketone, acetone, etc.

These may be used alone or in combination of more than one type.

Next, the present invention will be explained more concretely based on working examples.

## Working Examples, 1~8

A reactant (A-1) was obtained by reacting 113 weight parts (hereafter simply referred to as parts) of hydroxylmaleimide and 92.5 parts of epichlorohydrin and by using 44 parts of sodium hydroxide as a catalyst.

By using the reactant (A-1), compositions containing the ingredients indicated in Table 1 were prepared and were kneaded by means of an 8"φ 2-piece roll at 70°C/80°C for 10 minutes, and molding material compositions were obtained (ingredient ratio: weight part). All of them had excellent heat resistance and fast-curing properties.

Table 1

Working Examples	1	2	3	4	5	6	7	8
Reactant (A-1)	100	100	100	100	100	100	100	100
4,4'-diaminodiphenylmethane	5	10	20	40	60	20	20	20
Epoxy compound EP828	50	50	50	50	50	25	100	200
Dicyandiamide	5	5	5	5	5	5	5	5
Triethylamine tetraphenyl borate	3	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2	2
Epoxy silane KBM403	1	1	1	1	1	1	1	1
Silica powder	382	398	417	462	508	359	301	531
Indurative Bacore hardness (170°C, 2 minutes)	50	55	60	70	70	65	60	60
Bending strength retention (%)	95	100	100	100	100	100	100	90

## Bending Strength Retention

= (Bending strength (at 180°C) of sample after storing for 30 days at 200°C) / (Sample's initial bending strength (at 180°C)) × 100

## Working Examples, 9~15

A reactant (A-2) was obtained by reacting 125 parts of hydroxylethylmaleimide and 102 parts of epichlorohydrin and by using 44 parts of sodium hydroxide as a catalyst.

By using the reactant (A-2), compositions containing the ingredients indicated in Table 2 were prepared and were kneaded by means of an 8"φ 2-piece roll at 70°C/80°C for 10 minutes, and molding material compositions were obtained. All of them had excellent heat resistance and fast-curing properties.

Table 2

Working Examples	9	10	11	12	13	14	15
Reactant (A-2)	100	100	100	100	100	100	100
Epoxy compound ECN1273	50	25	25	25	10	10	100
4,4'-diaminodiphenylmethane	20	10	10	10	-	-	40
P-vinylaniline	-	10	-	5	-	-	-
Vinylester resin (bisphenol/methacrylate reactant)	-	-	25	25	40	60	-
Diallylphthalate	-	-	5	5	10	20	10
Dicyandiamide	5	5	-	-	-	-	3
Dicumylperoxide	-	-	0.5	0.5	0.5	0.5	0.3
Triethylamine tetraphenyl borate	3	3	2	2	2	2	2
Stearic acid	2	2	2	2	2	2	2
Epoxysilane KBM403	1	1	1	1	1	1	1
Fused silica glass powder	417	-	-	-	-	-	-
Indurative Bacore hardness (170°C, 2 minutes)	70	70	75	75	80	80	80
Bending strength retention (%)	100	100	100	100	96	94	100

#### Working Examples, 16~18

A reactant (A-2) was obtained by reacting 125 parts of hydroxylethylmaleimide and 102 parts of epichlorohydrin and by using 44 parts of sodium hydroxide as a catalyst.

50 parts, 100 parts, and 200 parts of DEN431 (epoxy equivalent: 172~179) were separately admixed as a phenol-novolac-type epoxy compound to 100 parts each of the reactant (A-2).

5 parts, 10 parts, and 20 parts of 4,4'-diaminodiphenylether were admixed to the above three types of compounds, and 3 types of compositions

were thus obtained.

These compositions exhibited solubility of 40% or higher not only in polar solvents such as N-methylpyrrolidone, dimethylsulfoxide, etc. but also in ketones such as methylethylketone, acetone, etc.

#### Working Examples, 19~22

A reactant (A-3) was obtained by reacting 185 parts of N-(P-hydroxyphenyl)maleimide and 92.5 parts of epichlorohydrin and by using 44 parts of sodium hydroxide as a catalyst.

By using the reactant (A-3), compositions containing the ingredients indicated in Table 3 were prepared, and their solubilities in various solvents were examined.

Table 3

Working Examples		19	20	21	22
Item					
Reactant (A-3)		100	100	100	100
4,4'-diaminodiphenylether		20	30	40	50
EP828 (epoxy equivalent: 175~210)		150	150	150	200
Dicyandiamide		5	5	5	5
Solubi- lity	N-methyl-2-pyrrolidone	○	○	○	○
	m-cresol	○	○	○	○
	Methylethylketone	40% or more	40% or more	40% or more	40% or more

#### Working Examples, 23~25

By using the reactant (A-1) of Working Examples, 1~8, compositions indicated in Table 4 were prepared and were kneaded by means of an 8"φ 2-piece roll at 70°C/80°C for 10 minutes, and molding material compositions were obtained (ingredient ratio: weight part).

Table 4

Working Examples	23	24	25
Compositions and Items			
Reactant (A-1)	100	100	100
4,4'-diaminodiphenylether	20	40	60
2-undecylimidazole	5	5	5
Stearic acid	2	2	2
$\Gamma$ -glycidoxypropyl trimethoxysilane	1	1	1
Fused silica glass powder	406	454	502
Carbon black	1	1	1
Indurative Bacore hardness (180°C, 2 minutes)	50	60	60
Bending strength retention (%)	98	100	100